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ION SELECTIVE MEMBRANE ELECTRODES FOR WATER POLLUTION MONITORING

STATE UNIVERSITY OF NEW YORK

PREPARED FOR
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Ion-Selective Membrane Electrodes for Water Pollution Monitoring

by

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Conclusions

1. The development of new membrane electrodes for ions not previously accessible to such measurements has been shown to be entirely feasible as exemplified by the design of carbonate and sulfate ion selective electrodes.

2. Micro and flow-through membrane electrodes can readily be constructed for both anions and cations by utilizing various configurations. These designs are eminently suited for continuous monitoring applications or measurements on restricted sample volumes.

3. By combining electrode potentiometry with chemical manipulation, the measurement capabilities of membrane sensors can be extended to non-electroactive materials by virtue of direct reaction or ion binding.

IV. New Electrodes and Potential Electrode Systems

Previous attempts to devise bicarbonate or carbonate ion selective electrodes have resulted in electrodes with poor selectivity for the desired ion with respect to such common interferences as chloride. We have now succeeded in preparing a liquid membrane electrode with selectivity for carbonate with respect to chloride, sulfate, and phosphate of at least 10^3 and negligible response to bicarbonate. The electrode yields Nernstian response to carbonate levels in the 10^{-2} to 10^{-6} molar range and has a response time of 30 sec. to 2 min. depending on the concentration levels employed.

The liquid membrane electrode is constructed in the conventional manner using plastic electrode bodies (Orion) and cellulose acetate support membranes with 0.1μm average pore diameter (Millipore Corp.) or Orion 92-20 membranes. The active electrode material is formed using a liquid phase consisting of 1% (by volume) of tricaprylyl methylammonium chloride (General Mills Chemicals, Inc., Aliquat 336) dissolved in trifluoroacetyl-p-butylbenzene. The latter is prepared by a Friedel-Crafts acetylation of butylbenzene with trifluoroacetic anhydride using anhydrous aluminum chloride as a catalyst, purified by fractional distillation, and identified by mass spectrometry (m/e 230), infrared spectroscopy, and nuclear magnetic resonance. The quaternary ammonium salt is used in the chloride form, as received, or converted to the bicarbonate form. An aqueous solution, 0.1 molar in both sodium chloride and sodium bicarbonate, is used as the internal electrode reference solution. All measurements are taken against a double junction Orion reference electrode.

Since carbonate coexists with bicarbonate in pH dependent equilibrium, the carbonate levels must be calculated using the relevant equilibrium constants (K_1 = 4.5×10^{-7}, K_2 = 4.8×10^{-11}) and the modified Davies equation. Our data indicate the absence of any response to the bicarbonate ion. Indeed, experiments carried out in mildly acidic media (pH < 5.5) where bicarbonate is vastly favored over carbonate, still yield potentials appropriate for a pure carbonate response even though the concentration of carbonate is less than 10^{-8} molar. In practical terms, however, the interconversion of carbonate with bicarbonate restricts the lower pH limit of the electrode to approximately pH 5.5. The electrode has an upper pH limit of approximately 8.5 at 4×10^{-3} molar carbonate and 9.5 at 5×10^{-2} molar carbonate.

Measurements carried out in mixtures of carbonate and chloride show negligible chloride interference even in samples containing 10^{-1} molar chloride and 10^{-5} molar carbonate. We calculate the carbonate to chloride selectivity to be 5.4×10^3. This value should be regarded as a lower limit because of possible residual carbonate levels in the chloride reagent used. Similarly, we have determined the carbonate to sulfate selectivity of the electrode as 6.7×10^3 and the carbonate to phosphate (taken as $HPO_4^=$) selectivity as 3.8×10^3.

The overall potentiometric behavior of the new electrode is typical of liquid membrane electrodes in general. We observe response times ranging from 30 seconds to 2 minutes in carbonate solutions, the slowest response being found at the lowest concentration levels. Electrical noise in carbonate solutions does not exceed 0.2 millivolts and reproducibility of $\pm$ 0.5 millivolts from sample to sample is readily achieved. Electrode lifetime in routine use will depend on factors such as the specific support membrane used and solution conditions but appears to be consistent with that reported for liquid membrane electrodes in general. In view of the dynamic range, selectivity, and other properties of this electrode we expect it to be useful for carbonate measurements in environmental systems.

Efforts to prepare useful sulfate ion-selective membrane electrodes have been largely unsuccessful. The work of Hirsch-Ayalon on $BaSO_4$-cellophane membranes, of Pungor and co-workers on precipitate impregnated silicone rubber membranes, and our own work on the Pungor electrodes showed that it is relatively easy to achieve potentiometric response to the sulfate ion but extremely difficult to obtain potentiometric selectivity for sulfate.

Recent progress on crystal membrane electrodes encouraged us to investigate pressed membranes on various crystal mixtures and we are now able to report on a new electrode with good response and selectivity for the sulfate ion. The electrode is relatively easy to prepare in the laboratory and has properties which suggest that it should be useful for analytical purposes.

Various inorganic salt mixtures, all based upon the use of Ag_2S as a membrane matrix, were pressed into membranes and evaluated for sulfate response. Typically, finely divided powders of the constituents were carefully mixed in known ratios and then pressed into membranes with a laboratory pellet press under controlled conditions of applied pressure, temperature, and pressing time. The resulting crystal membranes were then sealed into glass

or plastic electrode bodies and internally connected to a silver contact wire. Great care was taken to prevent surface contamination of the membranes.

Although a number of compositions gave membranes with sulfate response and greater or lesser sulfate selectivities, optimum results were obtained with membranes consisting of 32 mole % Ag_2S, 31 mole % PbS, 32 mole % $PbSO_4$, and 5 mole % Cu_2S. The most successful membranes were formed by pressing with an applied pressure of 102000 pounds per square inch for 18 hours at a temperature of 300°C. The elevated temperature appears to be the critical variable and may be related to the fact that Ag_2S undergoes a phase transition at 178°C. The small amount of Cu_2S in the pellet appears to improve the response time of the electrode membrane and may be related to the fact that Cu_2S has semiconductor properties.

Conditioning of the electrode surface appears to be important in giving optimum performance. We alternately soaked the electrode in dilute solutions of Na_2SO_4 and in mixtures of $AgNO_3$ and $Pb(NO_3)_2$ for periods of several hours. Occasionally, after prolonged experimentation under severe conditions, the shiny surface of the electrode became dull and performance was improved by gentle polishing with a wiping tissue or, in extreme cases, emery paper.

The principal results obtained with the sulfate membrane electrode indicate that the electrode yields a nearly Nernstian slope of 29 millivolts per decade (29.6 theoretical) over a fairly wide range of sulfate activity and, furthermore, displays appreciable selectivity for sulfate over a wide variety of common univalent anions. The electrode employed reached stable potential values in less than one minute in the sulfate solutions. Good electrode response is also obtained at sulfate concentrations greater than 10^{-2}M. For practical purposes, where empirical calibration curves are constructed or experiments are carried out at constant ionic strength, the electrode should be useful at least over the 10^{-1} to 10^{-4}M sulfate range.

Although the interference of the three halide ions tested appears to be related to the solubilities of the corresponding silver salts, we feel that it is not meaningful to compute numerical selectivity ratios for the ions tested on the basis of the present data. In our view, the small potential changes observed with large variations in concentrations of the univalent anions indicate that the electrode is essentially insensitive to these ions

and is primarily reflecting secondary activity, liquid junction, and membrane solubility effects.

Calibration curves were also constructed using sulfate salts with cations of various types and charges. The fact that these calibration curves were identical in slope and potential, indicates that the electrode is not responsive to cations. Preliminary experiments carried out as a function of solution pH showed little pH effect in the pH 3-10 range. At pH values below 2.5 there is a sharp potential change in the direction of apparent less sulfate; this is probably due to the formation of HSO_4^- in acid solution. Above pH 10.5 electrode response also deteriorates; we tentatively attribute this to hydroxide film formation involving the metal constituents of the membrane.

The mechanism of operation of this electrode is still obscure although the observation that best performance is obtained with membranes where the three principal constituents are present in a 1:1:1 ratio is provocative. It appears that the present electrodes possess sensitivity, selectivity, and response time properties suited to analytical purposes.

Neutral carrier type liquid membrane electrodes with selective response to monovalent cations have gained considerable acceptance in recent years because of their high selectivity coefficients. Neutral carriers include polyethers, polyesters, and certain antibiotics.

Typically, valinomycin is dissolved in an appropriate solvent such as hexane, octanol, or phenyl ether, and placed in a liquid membrane electrode assembly giving rise to an electrode with selectivity ratios of the order of 5000:1 for potassium over sodium; such a selectivity ratio is considerably higher than that of about 30:1 for cation sensitive glasses. Thus, an understanding of the electrode mechanism is important not only to make better electrodes but to improve understanding of ion transport in biological membranes.

In the latter connection, it must be recognized that the electrode consists of a solution of valinomycin in an organic solvent that is immiscible with water, interposed between two aqueous solutions containing the ions to be measured, just as the membrane of a living cell or of mitochondria separates the internal from the external solution of physiological character. In both cases valinomycin has been shown to greatly enhance the permeability of the membrane to potassium ions. Indeed, the selectivity of the valinomycin electrode is

comparable to that of biological membranes and it can be shown that some compounds with large anti-microbial activity are those for which complex formation constants with cations are high.

Various theories have been proposed to explain the role of valinomycin in ion transport through membranes. These mechanisms involve some complex formation between valinomycin and potassium ion. According to one model, the valinomycin molecule acts only at the phase interface to enable the ions to pass into the membrane wherein they move as free ions. A second model explains the enhanced permeability on the basis of channel formation involving the passage of ions through a channel of ordered valinomycin molecules which span the thickness of the membrane. The third mechanism, which we also favor, involves initial complex formation between the valinomycin and the cation followed by the transport of the ion through the membrane in the cavity of the valinomycin ligand, which acts as a "carrier" or transport catalyst. This model is also supported by the work of Eisenman et.al. on the actins. By measuring the potentiometric selectivities of the valinomycin electrode and the formation constants of the valinomycin-cation complexes, we showed that the selectivity coefficient is approximately equal to the formation constant quotient for various pairs of alkali metal ions; in thick electrode membranes similar results were also obtained when cyclic polyethers were used as carriers. Furthermore, we showed that ion selectivity is lost when the membranes are "frozen" even though some residual conductivity persists; this is taken to support the carrier model because we feel that freezing the membrane greatly reduces the mobility of the bulky carrier molecule and largely negates its transport catalyzing action in electrode membranes.

V. Micro and Flow-through Electrode Sensors

We have devoted a good deal of effort to the construction and evaluation of a series of microelectrodes of the type metal sulfide/silver sulfide, selective towards Ag^{+}, Cu^{2+}, Pb^{2+} and Cd^{2+}, as well as of the type silver halide/-silver sulfide, selective towards S^{2-}, Br^{-}, Cl^{-}, I^{-}. Electrodes constructed in our laboratory have tip sizes in the range of 50-100 microns and have been evaluated in solution volumes of between 0.5 and 1 microliter, although the dimension of the electrodes would allow use of sample volumes as small as 0.05 microliters.

All membrane materials were prepared by coprecipitation of silver sulfide and the corresponding metal sulfide (Cu, Cd, Pb) or silver halide (I, Br, Cl). In the case of the heavy metal electrodes appropriate volumes of 1 M silver nitrate and 1 M metal nitrate were mixed and added to excess sodium sulfide. In the case of the halide electrodes the appropriate weight of potassium halide was added to 1 M sodium sulfide and the stoichiometric amount of silver nitrate was then added to the mixture of sodium sulfide and potassium halide. The precipitations were carried out in the presence of excess sulfide and/or halide, and the metal nitrate solutions were always added to the potassium halide and/or sodium sulfide solutions.

The precipitate was very thoroughly washed with hot water, then with acetone, filtered and dried in air at about 100°C. A revised washing procedure used in special cases is detailed below for the lead and cadmium electrodes.

In general, membranes were pressed using a KBr die with a 13 mm diameter plunger. Approximately 2 grams of coprecipitate was pressed under vacuum at room temperature for various lengths of time under a 20,000 pound load, which corresponds to about 100,000 p.s.i. The lead and cadmium electrodes required pressing at elevated temperatures which were achieved by wrapping a heating tape (Briscoe Mfg. Co., Columbus, Ohio) around the die.

After removing the membrane from the die a silver wire was attached to one face using a silver-based conducting epoxy (E-Solder, Epoxy Prod. Co., New Haven, Conn.). A coaxial cable was soldered to the silver wire and was used as the input lead to the pH meter. After preliminary tests showed that the macro membrane functioned properly, the microelectrode tip was machined as desired. The central membrane section is cut from the pellet with

a jewelers saw and mounted in a 4 jaw lathe chuck. The pellet is shaped into a cylinder of 1/8" diameter using a very sharp cutting tool. It is then placed in a collet, reduced to a 1/16" diameter, remounted in a 1/16" collet and sharpened to a pointed tip using a shallow compound angle on the lathe. The micro sensing element was then put in a glass sleeve which was half filled with the conducting epoxy. A length of wire was inserted into the epoxy from the other end of the sleeve and the assembly was set aside to allow the epoxy to harden. Next, the entire assembly is cemented with an insulating epoxy into a 12 gauge stainless steel tube. A 14 gauge hypodermic needle is cut to a length of about 3 cm. and cemented into the other end of the stainless steel tube. The needle hub is threaded with a 10-32 tap and a microadaptor soldered to the wire leading from the membrane and screwed into the hub of the needle. The stainless steel tube acts as a shielding and is connected through the microadaptor to the shielding of the miniature coaxial cable leading to the pH meter.

A reference micro-salt bridge was prepared by drawing a glass capillary tube to a fine point (tip opening about 20 microns) and the tip bent so that the salt bridge capillary could be fastened to the ion-selective microelectrode to bring the two tips very close together. The micro-salt bridge was filled with 10% potassium nitrate solution using vacuum. Polyethylene tubing was attached to the glass capillary, filled with 10% potassium nitrate, and inserted into a small container which held the reference electrode and a few milliliters of the electrolyte solution. The position of the reference container had to be adjusted so that the hydrostatic pressure at the tip of the salt bridge would be small. However, it was important to maintain a positive pressure at the tip so that the very small sample drop was not siphoned up into the salt bridge.

Contamination, evaporation and the delicate nature of the electrode tips must be effectively dealt with when making ion measurements in dilute solutions in submicroliter volumes. Various types of simple sample holder designs have been successfully employed. One arrangement involved delivery of the sample using a very fine-drawn glass disposable pipette upon a fine nylon screen stretched over a small beaker. The microelectrode assembly was mounted vertically in a micromanipulator (Hacker Model M-1, Hacker Instruments, W. Caldwell, N. J.) with a precision three directional

mounting stage and maneuvered until the electrode tips just penetrated the surface of the sample drop. The nylon support is flexible enough so that no harm comes to the electrode tips if penetration is too deep. A number of sample drops can be placed in a small area on the nylon support and the electrodes moved conveniently from one drop to the next.

Evaporation of the sample was not a significant problem as long as measurements were taken within 3-4 minutes. Generally, all the electrodes reached a stable potential within 2 minutes but measurements can be recorded prior to this provided all readings in a particular series are taken at approximately the same time after insertion of the electrodes into the sample.

Evaluation of the electrodes was made with solutions prepared by successive dilutions of 0.1 M stock solutions. For the metal ion electrodes these stock solutions were prepared with the corresponding nitrate salts and for the halide electrodes the corresponding potassium salts were used. Potassium nitrate was used to adjust the ionic strength to 0.5 M and 0.2 M for the heavy metal and halide ion test solutions respectively.

Micro electrodes for silver (I) and copper (II) were relatively easy to produce. The silver (I) microelectrode was prepared from silver sulfide produced by the precipitation technique outlined above, whereas, the copper (II) microelectrode was prepared from a 50% mole ratio of copper sulfide/silver sulfide coprecipitate. The exact composition of the coprecipitate was not found to be a critical factor in electrode performance. Both the silver and copper electrodes were pressed at room temperature under approximately 100,000 p.s.i. for about 30 minutes. Variations in the presure and duration of the pressing did not significantly affect the response characteristics of the electrodes. Pressures as low as 70,000 p.s.i. and pressing time as short as 1 minute produced electrode membranes with Nernstian response. The response of these microelectrodes is reasonably fast. Instant potentials were usually within 5-10 millivolts of the final values reached within 30 seconds in sub microliter sample volumes.

Satisfactory lead (II) and cadmium (II) microelectrodes proved to be significantly more difficult to produce than the silver and copper electrodes. The composition of the lead electrode membranes was varied from 20-70% mole ratio lead sulfide/silver sulfide and the membranes

were pressed at 100,000 p.s.i. for different lengths of time varying from a few hours to 1 day. All membranes except the 20% pellet exhibited fracture planes parallel to the surfaces, apparently due to poor pressing characteristics of lead sulfide. The presence of a large percentage of silver sulfide, which has excellent pressing characteristics, in the 20% lead sulfide/-silver sulfide membrane prevented cracks from developing; however, the membrane showed no response to lead (II). This behavior was thought to be due to a lack of availability of lead sulfide at the surface of the membrane.

In order to incorporate a larger percentage of lead sulfide in the membrane and still prevent cracking of the pellet, the die was heated to approximately 150°C during the pressing operation. Silver sulfide exhibits a phase transition from the rhombic to the cubic form at 175°C under 1 atmosphere pressure. At the very high pressures used for pressing the pellets, e.g. about 6800 atmospheres, this transition should occur at a temperature well below 175°C. This phase change might allow for a more favorable packing of silver sulfide and lead sulfide to permit the use of higher lead sulfide ratios. Thus, a 50% mole ratio lead sulfide/-silver sulfide coprecipitate was hot pressed at 100,000 p.s.i. for about 3 hours. The membrane was not cracked when removed from the die and it was found to respond to lead ions. However, the slope of the calibration curve decreased continuously from a near Nernstian value in 10^{-1}-10^{-2} M lead nitrate solutions to less than 15 millivolts per decade at a concentration below 10^{-3} M lead nitrate.

X-ray diffraction studies did not yield much structural information about the lead sulfide/silver sulfide membranes, but did indicate the presence of as much as 3-5% of lead sulfate in the pellets. Since lead sulfate has a solubility product of about 10^{-8}, which is much larger than that of lead sulfide ($K_{SP} \sim 10^{-28}$), its presence in the membrane may be responsible for the poor response of the hot pressed 50% lead sulfide/silver sulfide membrane. Lead sulfate can form from moist lead sulfide at temperatures as low as 50°C and thus, might have been produced during the drying procedure.

Therefore, a revised washing procedure was used in order to eliminate the possibility of lead sulfate contamination. The coprecipitate was boiled for an hour, filtered, washed with dilute nitric acid and washed many times with distilled, deionized water and, then, dried in vacuum at room temperature. The precipitate is mixed with carbon disulfide and filtered, then washed with acetone and dried in air at 80-100°C.

A 50% mole ratio lead sulfide/silver sulfide coprecipitate prepared according to this method was hot pressed at approximately 115,000 p.s.i. for about 17 hours. This membrane had no cracks and, after calibration as a macroelectrode, was shpaed into a microelectrode which responded well to lead (II) at levels as low as 10^{-5}M in sample volumes of less than 1 microliter. The electrode responded within 10 seconds and stable potentials were reached in 2-3 minutes.

Similar preparative problems were encountered with the cadmium (II) electrode. However, using the revised washing procedure and the hot pressing technique ($\sim$ 150°C, 15-20 hours, and 115,000 p.s.i.), a 50% mole ratio cadmium sulfide/silver sulfide membrane was prepared which responded in a Nernstian fashion to cadmium test solutions. Membranes of this composition were very difficult to machine into micromembranes and the composition was finally altered to 25% cadmium sulfide/silver sulfide in order to improve the machining characteristics. A membrane of this composition was hot pressed as above and machined into a micromembrane which responded to cadmium solutions down to a concentration of 10^{-5}M and reached a steady potential within 1 minute.

For the preparation of bromide ion responsive microelectrodes, membrane material composed of 50% mole ratio silver bromide/silver sulfide was prepared as outlined. A membrane was pressed at room temperature under 100,000 p.s.i. for about 1 hour. The membrane showed no evidence of cracking and, after testing its response to bromide solution, in the macro form, it was machined and mounted as a micromembrane. The bromide microelectrode responded well in 0.5 microliter samples and reached a stable potential within 1-2 minutes.

The chloride electrode was produced using a 50% mole ratio silver chloride/silver sulfide coprecipitate prepared by the general procedure in the presence of slight excess of chloride. A membrane with Nernstian behavior was prepared by pressing under the same conditions as used for the bromide electrode for about 1 hour. It should be noted that during the machining of the pellet, prolonged contact between the membrane and the metal collet of the lathe tends to cause corrosion; this problem can be minimized by coating the metal parts in contact with the membrane with a teflon spray. After machining, the micromembrane was incorporated into an electrode body and found to respond with a theoretical slope to chloride levels above 5×10^{-4}M chloride;

at lower concentrations the slope begins to decrease in the same fashion as for the commercial macroelectrode. It is of interest to note that another 50% silver chloride/silver sulfide coprecipitate, prepared with excess sulfide and chloride, is responsive to silver (I) but not to chloride.

Considerable difficulty was encountered during attempts to prepare iodide sensitive microelectrodes using the procedures just detailed. Electrodes obtained displayed sub-Nernstian response or poor stability during prolonged use. These problems were ultimately traced to incompatibility of the membrane material with the silver epoxy used to make electrical contact and to the need for proper conditioning of the electrode tip.

Successful iodide microelectrodes were finally realized by pressing 50% silver iodide/silver sulfide coprecipitates, prepared in the presence of excess iodide, at room temperature and an applied pressure of 115,000 p.s.i. for 1-1/2 hour periods. After machining, the microelectrode was mounted in a glass tube equipped with a permanently sealed silver-silver (I) liquid internal reference. With conditioning in 0.1 M iodide solutions and gentle polishing of the tip before use, this electrode yields excellent Nernstian behavior over wide iodide concentration ranges and has excellent reproducibility. The iodide electrode is the only microelectrode of this set which is not completely solid state, although the sealed internal reference solution requires no attention during normal use. It seems likely that further investigation of conductive cementing materials would result in a suitable procedure for constructing a completely solid state version.

The general properties of the heavy metal and halide electrodes described are quite similar to those of commercial macro electrodes in terms of range, selectivity, and dynamic characteristics. In view of the low cost and relative ease of preparation of these electrodes, it is hoped that such microprobes could find use in analytical and environmental measurements where sample sizes are the restrictive limitation.

The importance of ion selective electrodes in many aspects of chemistry has been demonstrated by the rapid increase in the volume of literature on the subject over the last few years. As a result, the characteristics of the many electrodes available for a large number of ions have been well documented in this period. The applications which have been proposed cover a range

from enzyme assays to pollution analysis. In the vast majority of such applications, electrodes are used in the dipping mode with relatively large sample volumes. Relatively few sensors have been developed for use in small volume flowing streams and so far these have been only of the liquid membrane or glass capillary type. Electrodes of this type for Na^+, K^+, Ca^{++}, and Mg^{++} are commercially available and the utility of such electrodes for measuring a number of rate constants using a fast flow system has been demonstrated. A method by which solid membrane electrodes could be incorporated into such a system using a cap device greatly reduces the necessary flowing volume while using a regular dip-type sensor. There is no doubt that where sample volume is restricted and automated determinations of a large number of samples is desired such a system is both convenient and reliable. We also dealt with the construction, treatment and characteristics of solid membrane flow through sensors where the test solution is channeled through the sensing membrane and not merely across its surface. The advantages of this technique are substantial reduction in sample volume and the possibility of determining several ions by a series of sensors placed close together, the flow being led directly from one to the next with a common reference electrode. We have succeeded in preparing and evaluating flow-through sensors for several heavy metal ions. Optimum results are shown to depend upon careful attention to the physical construction of the electrodes, the choice of preparative procedures, as well as the polishing and conditioning of the membrane surfaces. Specific procedures and methods are proposed to facilitate the construction of such flow-through sensors in other laboratories and the results of our evaluations are presented.

Many methods of preparing the metal sulphide membrane materials have been suggested, from coprecipitation by various techniques to direct reactions between metals and sulphur.

Individual precipitation of sulphides from sodium sulphide and metal nitrate solutions, followed by thorough mechanical mixing in the desired ratio proved quite successful in some cases but reproducibility was not sufficient for our purposes. Using the direct reaction technique preparations of single and mixed sulphides in our trials led to highly unsatisfactory membrane materials giving very limited or no response to the ion in question. This could have been due to the difficulty in maintaining the proper excess of sulphur during the high temperature reaction because of the volatility of sulfur. Overall, the most reliable technique was bulk coprecipitation as recommended in the ORION patent. All electrodes discussed in the

following sections were therefore prepared from membranes pressed from materials produced by this procedure. The method involves mixing the metal ion solutions and adding this mixture to a slight excess (~ 10%) of sulphide solution with constant stirring to assure that an excess of sulphide ions is present throughout the precipitation procedure - an important requirement. To obtain finely divided powders, rapid mixing of relatively concentrated (1M) solutions was used, the process being carried out below 20°C. The precipitate was then thoroughly washed several times with hot and cold deionized water, dilute nitric acid, carbon disulphide and acetone before being dried at 80°C in air. Proper washing and drying was critical since any contamination with metal ions or other salts caused insensitivity in the resulting electrodes. For lead sulphide - silver sulphide coprecipitates, drying in vacuum is recommended since, in the presence of air and moisture, lead sulphide is rather easily converted to lead sulphate. The presence of this compound in some batches of precipitates was confirmed by x-ray diffraction analysis and the resulting membranes gave unsatisfactory electrodes.

In all cases a 1:1 mole ratio of silver sulphide to metal sulphide was found to give best results though other ratios between 1:4 and 7:3 produced fairly good sensors.

Of the many methods of preparing membranes based on heavy metal sulphides the most useful in this case is the pressure forming of polycrystalline pellets. Such pellets are rigid and, therefore, easy to handle but are soft enough to be conveniently drilled and machined with normal tools.

While pressures of 100,000 p.s.i. maintained for periods of a few minutes were sufficient to produce good cupric ion electrodes, such cold pressings of cadmium and lead coprecipitates gave pellets without any response to the ion in question. Increase of pressing time and pressure to 155,000 p.s.i. did not improve this situation. Cold pressed Ag_2S/PbS pellets, in fact, did not even hold together very well and readily split into thin circular plates. Hot pressing of these materials, on the other hand, had a pronounced effect on the performance of the resulting electrodes. Temperatures above 100°C during pressing produced much more robust pellets which did respond to concentration changes. Optimum pressing times and temperatures for both cadmium and lead pellets were 4-8 hours at 150°-250°C. Pressures greater than 100,000 p.s.i. showed no beneficial effect nor did times in excess of eight hours. When temperatures higher than 250°C were used, layers of silver metal were formed on the sur-

faces of the pellet indicating perhaps some decomposition of the silver sulphide. These membranes made unsatisfactory electrodes though their performance could be slightly improved by heavy sanding of the surface.

For all 13mm pellets, between two and three grams of material were pressed to give pellets approximately 3mm thick. In the case of 5mm membranes proportionately less material was used. Dies were evacuated throughout the pressing period using a Duo-Seal Model 1400 vacuum pump (W. M. Welch Co., Chicago, Ill.). The different conditions required to produce good lead and cadmium membranes can be rationalized with the fact that, while copper and silver sulphides readily form solid solutions, the other sulphides do not. Silver sulphide is known to undergo a phase transition at 178°C; perhaps temperatures in this region are required to form a suitable lead or cadmium sulphide - silver sulphide mixture. Simultaneous heating and pressing are necessary, however, as cold pressing followed by heating at 200°C for four hours in air or nitrogen failed to produce responsive membranes. Pellets treated in this manner blistered and could not be sanded down to give a smooth surface.

We have developed two methods of achieving suitable direct internal contacts. The first uses a silver filled epoxy (E-Solder R, Epoxy Products Co., New Haven, Conn.) to join a silver or copper wire directly to the pellet. On curing this epoxy forms a strong conductive bond between the silver sulphide of the pellet and the metal wire. Best silver particle to silver sulphide contact is achieved if the membrane surface is lightly sanded and well cleaned before application of the epoxy. The second method involves pressing a thin layer of silver powder followed by a layer of copper powder (M.C.B. Manufacturing Chemists, Norwood, Ohio) on top of the coprecipitate during pellet preparation. A copper connecting wire can then be soldered to the copper layer or affixed with conductive epoxy. The latter means is perhaps more satisfactory since the heat induced expansion involved in soldering can cause the metal layers to separate from the pellet. When the membranes are mounted as discussed in the following section, the internal contacts are well protected from the sample solutions.

A number of factors are involved in the choice of the best method of mounting the pellet. If, as was the case in our initial work, performance figures for the electrode used in the dipping and flow-through modes are to be compared, the membrane cannot be totally enclosed in the electrode body. The pellet, with the connecting wire attached, is sealed with Araldite ^{R} epoxy resin into one

end of a Plexiglas tube. Contact surfaces should be sanded before sealing. Alternatively, the electrode body can be filled with Bio-Plastic [R] polymer (Ward's Natural Science Est., Rochester, N. Y.) which, in addition to sealing the membrane to the body, makes the final electrode more robust. At the other end of the Plexiglas tube the connecting wire terminates in a B.N.C. connector. There is no necessity to shield this wire.

For an electrode to be used only in the flow-through manner a second mounting technique is recommended. The entire pellet and connecting wire are embedded in Bio-Plastic using a circular mold. In this way, contamination of the pellet and wire are avoided. In this case, the flow channel is drilled in the longitudinal axis of the pellet and the internal connection is made to its circumference. Obviously, pellets with silver and copper layers are not suitable for mounting in this manner. Again, sanding of all pellet surfaces before embedding improves the seal of the plastic to the membrane. This technique allows several pellets to be mounted in the same embedment so that a series of sensors can be made in one continuous block.

After final cure, the polymer can be machined to a convenient size and shape and any protruding connnecting wire protected by a Plexiglas tube. This configuration also lends itself to the use of an internal filling solution since the seal is good enough to keep internal and flowing solutions separated even under the high pressures of fast flow conditions.

The flow channel in the membranes was made by relatively slow speed drilling with a regular steel drill bit of suitable diameter. Depending on the application envisaged and the thickness of the pellet, holes of 0.025 inches to 0.075 inches in diameter were drilled. For laterally channeled pellets the sensing path is relatively long, up to 13mm, and hence smaller holes are preferable. If, however, the electrode must measure activity at more precise points in the flowing stream the second configuration is more suitable. This gives a short sensing path which can be less than one millimeter depending only on the thickness of the pellet. Hence, larger holes and faster flow rates are possible without making the dead space within the membrane very large. During drilling great care must be exercised so that the seal between the body and the pellet is not fractured. Even the slightest separation will permit solution to enter by capillary action and such contamination is very difficult to remove. In addition, no lubricant oil was used as it was found that this irreversibly contaminates

the membrane surface.

It had been noted initially that fine polishing of membrane surfaces greatly improved the response times and sensitivities of dip-type electrodes. Such treatment proved to be even more important in the case of flow-through electrodes as will be detailed below. Effective polishing of the narrow channels was achieved using a fine cotton-covered wire or needle soaked in water and impregnated with diamond dust. Oil based diamond pastes, while more efficient, contaminated the channel and virtually destroyed response.

When used in the dipping mode, all electrodes exhibited Nernstian response in the 10^{-1}M to 10^{-5}M concentration range. The copper electrode remained Nernstian to 10^{-6}M while the cadmium and lead models seldom gave better than 16-18 mv change between 10^{-5}M and 10^{-6}M. In the flowing mode each electrode closely reproduced its dipping behavior provided surface pretreatments were performed. Absolute potential values were found to vary as much as 30 mv from pellet to pellet. Perhaps part of this could be attributed to minor variations in the internal contacts but the major portion seemed to be due to surface treatment differences and inherent properties of the pellets. Evidence that the latter was most important was gained when two copper electrodes were made from the halves of a single pellet. These displayed identical potentials ($\pm$ 0.2 mv or better) throughout the 10^{-5}M to 10^{-1}M range when directly compared in the same solutions.

Polishing to a bright mirror finish proved to be the single most effective method of producing a substantial improvement in electrode behavior. For cadmium and lead sensors the difference in both response time and flow rate dependence was very marked. Not only is the equilibrium potential reached much more rapidly (less than 5 sec. compared to almost one minute) but the potential change is much more nearly Nernstian. In addition, the at rest potential is almost the same as that of the flowing stream. Flow rates in each case were 1 ml sec^{-1}.

We have, thus, shown that a number of solid membrane flow-through electrodes can be made in the laboratory. Silver sulphide based membranes for chloride, bromide and iodide ions have also been successfully prepared and we expect the range of ions which can be sensed in this manner to be quite large. Applications of such sensors could include continuous process or auto-analyser effluent monitoring and fast flow kinetic studies. In the former case, it is quite feasible that several ions could

be monitored by casting a number of different membranes into a single plastic block; if several idential pellets were arranged in this manner, the progress of a reaction could be followed at various stages in a single stream.

We also developed a novel split crystal membrane electrode which permits almost perfect matching of electrode characteristics and allows "double beam" measurements to be made by simultaneously operating one side of the split electrode as a reference and the other as the indicating electrode. Aside from the convenience of having matched electrodes, this new system has the important advantage of minimizing the need for restandardization with changes in conditions or in prolonged use. This desirable feature results from the fact that the split sensor is formed from a single membrane which undergoes uniform aging with time, specific use or temperature changes.

Although the general principle of the split membrane approach should be applicable to many membrane electrodes, we selected the Ag_2S/AgI type iodide sensor for detailed study because of our previous experience with this electrode and its known reliability. When used in the differential mode, the split membrane sensor eliminates the need for an external reference electrode and should be useful for continuous monitoring, automated analysis, and process control.

Coprecipitated AgI/Ag_2S powder was prepared and pressed into a wafer thin disc membrane (13mm diameter by 0.7mm thickness). The disc membrane was then split to give two semi-circular membranes which were embedded together in one Bio-Plastic mold. The two half membranes were embedded side by side but not in contact. A flow channel was drilled through each split membrane and connnected to polyethylene tubing of appropriate diameter. The flow channels were polished with diamond powder to improve the response of the electrodes. Internal contact to the membrane was made by drilling a hole at the edge of the plastic body to the membrane and attaching a piece of plexiglass tubing. $AgNO_3$ (0.1M) was placed in the side arm to provide liquid contact with the membrane. A piece of silver wire attached to a BNC connector completed the circuit for each arm of the electrode.

Each split electrode membrane was first calibrated in a flowing stream against an external reference electrode using a series of KI solutions of ionic strength adjusted to 0.3M with KNO_3. The two electrode halves were calibrated simultaneously at room temperature ($21 \pm 1°C$).

In the differential mode, a solution of known iodide concentration was passed through one of the membrane halves which served as the reference electrode. Solutions of varying iodide concentrations were passed through the other membrane (sample electrode), and the potential differences between the two electrodes were measured with the differential amplifier. The recorder was used to record the potential differences as well as to measure response times.

The readings at each iodide concentration agree to within one millivolt. The critical factor in determining matched potentials does not depend so much on the electrode membrane but rather on the internal electrical contact, i.e. the filling solution, silver wire contact and B.N.C. connections must be identical. The silver wire leads had to be lightly sanded to remove any coatings and good tight fits of the silver wires into the B.N.C. connections were essential for matched readings.

The potential readings varied from day to day with the indicated difference being the non-cumulative drift that normally results from such external factors as temperature changes, junction potentials and membrane conditioning. Although the potential readings varied, the response of the two electrodes remained matched and the response slope remained constant (57.3 $\pm$ 0.4mV) for each calibration. This is an important factor for possible use of the split electrode system as a continuous monitor. The system may be used over a long period of time since the response of the matched membrane electrodes will not be affected by normal changes in external factors. The electrodes change in exactly the same manner and, thus, the need for frequent standardization is eliminated. We have used the electrodes over a period of three to four weeks with no deterioration in performance.

In the dual flow differential experiments, the same iodide solution was initially passed through both electrode membranes. Because the two membranes are matched to < 1mV, the resultant differential reading was always found to be less than 1 mV. Then, one side of the electrode (I) was used to measure a series of iodide solutions while the original solution continued to pass through the other electrode (II) serving as the reference. The potential differences between the two electrodes were recorded for each iodide solution and were found to give a straight line calibration plot. The electrodes were then operated so that electrode I was now the reference and electrode II was the sample electrode with very similar results.

The concentration of the referenece solution (10^{-5} M to 10^{-1} M KI) was found to have no effect upon the response or performance of the sample electrode. In a series of consecutive runs, using electrode I as the sample side, the replicate calibration slopes were 57.6 $\pm$ 0.6mV while

electrode II gave a slope of 57.3 ± 0.6mV. When consecutive runs were performed using electrode I as the sample and, then with electrode II as the sample, the slope values were found to agree within 0.3mV per decade.

It is clear that the results obtained are consistent with the degree of electrode matching achieved. At the present time, such matching of the two electrode halves includes agreement of E° values to <1mV, agreement of calibration slopes to <0.3mV, and comparable response times. Most important, this degree of matching appears to be unchanged with time over the four week period studied. Thus, the novel electrode configuration described should be useful for differential potentiometry under a variety of conditions.

VI. Applications Methodology

Because of concern over water pollution problems related to the growth of aquatic vegetation, materials such as nitrilotriacetic acid (NTA) are being substituted for phosphates in detergents. As a result there is a great need for new analytical methods to determine NTA in the presence of common detergent constituents. Previously, NTA has been determined by thermometric titration and by titration with copper(II) using azurol S as indicator after removal of phosphates by precipitation. We developed an electrode method, which permits the direct determination of NTA by copper(II) potentiometric titration without prior separation of phosphates, sulfates, or sulfonates.

A weighed amount of NTA was diluted with distilled-demineralized water in a 100 ml volumetric flask. An aliquot was added to the thermostatted cell, 5 ml of 1 M NH_3-NH_4NO_3 buffer was added and brought to 50 ml with water so that the NTA was 0.001 M. The solution was stirred constantly by means of a Teflon coated magnetic stirring bar. The electrodes were inserted into the solution and the sample titrated with 0.01 M copper(II) nitrate. Potentials were recorded on a Beckman pH recorder. Investigation of interfering materials was made by weighing them directly into the original NTA solution.

Typical titration curves for the titration of NTA in NH_3-NH_4NO_3 buffer (pH $\sim$ 9.6) at various concentration levels show that NTA may be titrated directly at concentrations as low as 5×10^{-5} M under these solution conditions.

Since NTA is commonly used in detergents in combination with triphosphates, the effect of this constituent on the NTA titration was investigated. While the increasing concentrations of triphosphate decrease the total potential change of the titration, the position of the end point is not changed over the range studied. Thus, NTA can be titrated in the presence of triphosphate without prior separation.

Comparable experiments carried out in the presence of sulfate or sulfonate gave similar results and showed that sulfate shifts the position of the titration curve but does not alter the location of the endpoint.

Additional experiments carried out on commercial detergent samples known to contain phosphate and sulfonates also showed that NTA could be determined in such mixtures using the proposed method. Thus, it appears that the potentiometric titration of NTA with copper(II) as monitored by the copper ion-selective electrode should be useful for analytical purposes as the use of NTA in household products continues to increase.

Copper(I) ions are stable in a number of organic solvents, e.g. acetonitrile and nitromethane. The stability of copper(I) ions in such solvents has been explained by an increase of the solvation energy of copper(I) ions and/or a decrease of the solvation energy of copper(II) ions with respect to the solvation energies of these ions in water.

In this work the formation constants of copper(I) complexes with the halides and with thiourea in acetonitrile have been measured using a novel cuprous sulfide-membrane ion-selective electrode as the indicator electrode.

The membrane (diameter: 13mm) was prepared by heating finely powdered cuprous sulfide (Alfa Inorganics) (1.7-2.0g) at 300°C for 24 hr. under a pressure of about 7 ton/cm^2. After fastening a copper leading wire directly to the membrane, the pellet was imbedded in a glass tube with araldite (which proved to be very resistant towards acetonitrile) and the electrode surface was polished with very fine abrasive cloth. The electrode was then conditioned overnight in a 10^{-2}M copper(I) perchlorate solution in acetonitrile before the measurements were started.

The replacement of the internal electrode and filling solution, normally used in glass electrodes and ion-selective electrodes, by a direct leading wire contact to the membrane proved to be useful for the preparation of several sulfide-based solid state ion-selective electrodes. Leakage of the solution through the side-wall of the membrane and the electrode body, causing electrical contact between the solution and the leading wire and resulting in breakdown of the electrode, is almost totally excluded and facilitates use of such electrodes in non-aqueous solvents.

All experiments were carried out in a double-walled borosilicate glass vessel thermostated at 25°C. Electrodes and burettes were inserted through a rubber stopper in the cell. No special precautions were taken to avoid the entry of oxygen in the cell since the solutions were found to be stable towards air oxidation during the time needed for the measurements.

Potentiometric measurements (± 0.1mV) were carried out with a Corning Model 12 research pH meter. In solutions containing tetraethylammonium perchlorate as the supporting electrolyte both a Beckman quartz fiber type SCE filled with sat. KCl-methanol electrolyte or an Orion Model 90-02 double junction electrode with the supporting electrolyte solution in the outer chamber were used as a reference. In solutions containing sodium perchlorate as the supporting electrolyte however, stable potentials could be obtained only with the double junction electrode as a reference.

Calibration curves were recorded by adding increments of a 10^{-2}M or a 2.5 x 10^{-2}M copper(I) perchlorate solution to a known volume of solution containing the supporting electrolyte. Micro-burettes used for calibration or titration were graduated to 0.02 ml (for recording calibration curves a microsyringe was used for the lower concentrations). In complex formation studies the electrode was calibrated prior to each titration run.

For complex formation studies with chloride the total copper(I) concentration was held constant at $\sim$ 5 x 10^{-3}M during the titration by adding the same amount of copper to the titrant. For complex formation studies with bromide or iodide the total copper(I) concentration was $\sim$ 10^{-3}M and thiourea titrations were performed at different total copper(I) concentrations varying from 5 x 10^{-4}M to 5 x 10^{-3}M. The ligand concentration was varied over the range zero to 10^{-2}M for the halides (except chloride) and from zero to 2 x 10^{-2}M for thiourea.

The electrode displayed an almost Nernstian response to copper(I) ion concentrations over the range 10^{-2}M - 10^{-5}M with a slope of 55-56 mV/decade (theoretically 59.16 mV at 25°C). It was found that the slope decreased and the response time increased when x in $Cu_{2-x}S$ was varied from 0.21 to zero, the best results thus being obtained for $Cu_{1.79}S$. The cuprous sulfide used in this work had an almost perfect stiochiometric composition (analytical data supplied by the manufacturer), so that the small deviations of the slope from the theoretical value can be accounted for by the high metal to sulfur ratio of the membrane. No detailed study was made of the response time of the electrode. It was observed, however, that less than 60 seconds was required to obtain steady potentials for copper(I) concentrations > 5 x 10^{-4}M. Below this concentration level the response became more sluggish and an interval of 5-10 min. was allowed for equilibration. The E° values changed by several millivolts from one day to another but remained constant during the time needed for a titration run.

Our studies indicated that the electrode showed an almost Nernstian response, i.e. slope of 55-56 mV, for copper(I) concentration down to at least 3 x 10^{-7}M in the presence of complexing ligands.

The electrode was used for the measurement of the stepwise formation constants of copper(I) complexes with the halides in acetonitrile. Log β_1 and log β_2 values were as follows: Cl^-, 4.9 and 10.7; Br^-, 3.8 and 7.8; and I^-, 3.2 and 6.4. The electrode might be particularly useful for the study of interactions of copper(I) ions with organic ligands in acetonitrile. As an example, complex between copper(I) and thiourea has been investigated. The experimental data suggest $Cu[S=C(NH_2)_2]_2^+$ as the predominant complex species for which the formation constant has been evaluated as log β_2 = 6.3.

VII. Publications

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